

Characterization of modified Ti6Al4V alloy after fretting-corrosion tests using near-field microscopy

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Abstract

Fretting wear and corrosion of Ti6Al4V alloys at the bone/implant stem interface produces the release of wear particles and corrosive ions from the stem into the surrounding tissue that can induce bone resorption. In this work, oxidation treatments at 500° and 700 °C for 1 h have been studied for increasing the friction-corrosion resistance at these interfaces. The friction-corrosion process of thermally treated Ti6Al4V discs against pins of cadaver bone were evaluated in bovine serum medium for 1 million cycles of loading at 4Hz with maximum contact pressures of 10 MPa. Cyclic displacement of 120 µm for pin-on-disk samples in a linear motion was applied. Samples were characterized, before and after the oxidation treatment, by atomic force microscopy (AFM), scanning Kelvin probe (SKP) and scanning electrochemical microscopy (SECM). The characterization of the Ti6Al4V samples showed the growth and the different morphology of the oxides as a consequence of the temperature. SKP and SECM revealed that the surface of oxidized samples had lower

electrochemical activity than as-received surfaces. After the fretting-corrosion test, the thermally treated samples showed low electrochemical reactivity; specifically oxidation treatment at 700°C revealed that the rutile scale formed potentially improves the performance of Ti6Al4V in fretting-corrosion against bone.

1. Introduction

Titanium and its alloys are considered biocompatible and corrosion resistant, with Young's modulus closer to the bone, compared to other metallic biomaterials. However, the wear resistance is poor compared to other metals used in biomedical applications. Therefore, titanium alloys are no longer used for bearing surfaces, but they are widely used for femoral stems, acetabular cup shells and other orthopedic prostheses, designed to be implanted directly against bone. Unfortunately, small amounts of micromotion of bone against titanium and its alloys can potentially generate substantial amounts of titanium debris, as a result of micro-motion and fretting wear [1, 2]. Fretting appears at a relatively small scale (less than 200 μm) motion induced by cyclic loading at the bone/metal interface of implants. The generation of ionic and particulate debris comes from the fracture and abrasion of the metal passive oxide films that are deposited in the local tissue. This release has caused clinical concern due to the known potential toxicities associated with some elements included in implant alloys as well as known pathologies such as particle induced inflammation and hyper sensitivity associated with the degradation of the metal implant. In addition, metal concentrations can be found in tissue taken from the region around Ti alloy prostheses [3, 4, 5].

The poor tribological properties of titanium and its alloys are due to its low resistance to plastic shearing and the low protection offered by the passive film [6]. This type of fretting/wear has not been studied sufficiently in the literature. Recently, some researchers have studied bone-metal fretting/wear but their models have had shortcomings; for example, the loads and the motions were not physiologically accurate [7, 8]. That is why one of the aims of the present work is to research this type of bone-titanium alloy fretting wear in a laboratory model, dealing with titanium alloy orthopedic implants, such as hip and knee replacements.

In the literature several studies have been carried out in order to improve the tribological performance of the Ti-based alloys [9,10,11,12]. These studies mention the development of new Ti-based alloys in order to decrease the Young's modulus and to increase the wear resistance [13], as well as the application of coatings to increase the hardness and tribological behavior of metallic surfaces [14].

The oxidation treatment at high temperature of Ti-based alloys has been shown to be a promising surface modification technique for providing higher protection against wear and friction [15, 16, 17, 18, 19, 20]. The oxidation treatment of Ti-Al alloys has been widely studied in the literature [21, 22]. The addition of aluminum to titanium enhances the oxidation resistance at 700 °C since aluminum reduces the solubility of oxygen in α -Ti from 34 at.% to 0.3 at.% [23]. A α -Al₂O₃ layer is found near the external interface, either in the alpha or gamma form and alumina is distributed in distinct sublayers of variable thickness.

The oxidation treatments on Ti6Al4V alloys not only produce the formation of mixed Ti and Al oxides on the surface but also the named Oxygen Dispersion Hardening (ODH)

zones [17]. Above 200 °C, the thickness of the oxide layers significantly increases while ODH zones develop above 400 °C. At temperatures above 600 °C, the increase in oxidation rate causes the formation of thicker but defective oxide layers leading to easy penetration of oxygen into the substrate. Applying thermal oxidation to titanium and its alloys creates a relatively thin mechanically stable Oxide Layer (OL), supported by the ODH oxygen diffusion zone for successful surface protection at room temperature that increases the hardness of the subsurface below the oxide layer.

The aim of this work is the near field characterization of TiAlV surfaces, thermally oxidized at 500 and 700 °C for 1 h, after the friction-corrosion test in a laboratory model of the TiAlV/cortical bone couple under near physiological conditions. The characterization of the worn surfaces was done by localized techniques using the Atomic Force Microscope (AFM), Scanning Kelvin Probe (SKP) and Scanning Electrochemical Microscope (SECM).

2. Experimental procedure

The material used in this research was the Ti6Al4V (wt%) alloy in the shape of disks of 30 mm diameter. Before oxidation, all major surfaces were abraded on fine silicon carbide papers and then mechanically polished with 1 µm diamond paste to achieve a mirror-like finish. Specimens were washed in running water, and ultrasonically cleaned with alcohol. The oxidation treatment was performed on Ti6Al4V disks at 500 °C and 700 °C for 1 h, in air. After oxidation, samples were cooled in the furnace.

Pins of 6 mm diameter and 3 mm height were extracted from a diaphyseal cortical fresh frozen human cadaver bone (Figure 1a). After that, the pins were smoothly polished to obtain a flat surface. The final bone surface to be tested against the metallic samples is

shown in Figure 1b. The dark zones correspond to cancellous bone remaining in trabecula. Each pin was rinsed, cleaned, drilled and fixed in cement in order to carry out the friction-corrosion test, shown in the front view of Figure 1c.

The Ti6Al4V surfaces were characterized by means of X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM), Scanning Kelvin Probe (SKP) and Scanning Electrochemical Microscopy (SECM).

2.1. Fretting-corrosion test

The fretting wear simulator used, mounted in a MTS 812 servohydraulic load frame (MTS Corporation, Minneapolis, MN), includes three pin-on-disk assemblies located at 120° from each other in a horizontal plane (Figure 2). Fretting motion is produced by applying a bending moment to each of three vertically orientated cylindrical rods. The vertical load applied by the actuator is shared equally by all the bending rods. A metal Ti6Al4V disk was mounted on each of the disk holders fixed to the base plate. The base plate is mounted on the hydraulic actuator through a ball joint in order to distribute the load equally among the three test specimens. The bone pins embedded in cement and fixed in actuators (see experimental scheme) face downward so that the fretting surfaces are completely immersed in a chamber of 90% bovine serum lubricant. Details of the procedures followed in the fretting-corrosion experiments, as well as the equipment used are provided elsewhere [24]. Three Ti6Al4V samples of each condition: as-received, 500 °C and 700 °C for 1 h, acted as metal disks. Each bone pin was orientated in the fretting wear simulator so that the longitudinal axis of the bone shaft before cutting was parallel to the direction of motion. Fretting corrosion tests were carried out for 1 million cycles at 4 Hz with peak (maximum) compressive stresses (that is, contact pressures) of 10 MPa. The load profile in each cycle

applied to the MTS 812 servohydraulic load frame was adjusted to follow a double peak curve simulating walking, specifically a Paul's curve commonly used in hip joint simulator wear tests (Figure 3) [25]. The load profile corresponds to the pace of a man who weighs 70 kg. Cyclic displacements for pin-on-disk assemblies ranged from 100 to 120 microns, varying with the changing frictional properties at pin-on-disk interfaces during fretting testing.

2.2 Surface Characterization

The different phases of the surface of the thermally treated samples were identified from the X-ray diffraction (XRD) patterns obtained using a Siemens D5000 diffractometer employing Cu K α radiation, running at 40 KV/30 mA in the 2θ range 1° to 70° with a step size of 0.05° .

The surface of the Ti6Al4V disks in as-received condition and thermally treated at 500°C and 700°C were imaged by atomic force microscope (AFM) by using an Agilent 5500 AFM/SPM microscope in tapping mode. Information about the growth and morphology of the oxides, formed at the different thermal treatments and after fretting-corrosion tests was obtained in an area of $5 \times 5 \mu\text{m}$, while maintaining a constant height of $10 \mu\text{m}$ with respect to the surface.

The characteristics of the surfaces were studied through the topography, 3D images and height line profile. The height line profile and 3D images were obtained simultaneously from the simple flattened topographical image. Additionally, the surfaces were studied in terms of the height line profile in a specific area (indicated by a gray line in the 3D topographical image) and surface roughness. The average height is the mean absolute value of the surface based on the difference in height between peaks and valleys of the surface

obtained from the height line profile. In addition, the arithmetic average (Ra) and the root mean square (RMS) of the absolute values of all points of the profile were calculated.

The Vickers microhardness measurements were performed in a Wilson equipment. The microhardness was performed using depths of 1, 2, 5 and 25 μm . At least five measurements were made on each sample. Taking into consideration the relative large scattering associated with the small load and in order to minimize the experimental error, microhardness measurements were performed by consecutively the same operator and during the same period of time. The microindentation tests were conducted with a diamond Berkovich tip using a NanoIndenter XP from MTS Systems Corporation (Oak Ridge, TN) with a CSM module of continuous stiffness measurements. The indentations were carried out in displacement control, using an indentation depth limit of 1000 nm and a surface approach velocity of 10 nm/s. Once the surface was reached, there was a dwell period of 10 s. Hardness, H, and elastic modulus, E, were calculated from the load and displacement curves using the Oliver and Pharr method [26]. The final data were the mean of a nanoindentation matrix, from 80 to 100 indentations for each material, depending on the results obtained.

2.3 Surface reactivity Evaluation

The electrochemical reactivity before and after fretting corrosion tests was evaluated by Scanning Kelvin Probe (SKP) and Scanning Electrochemical Microscope (SECM).

The Ti6Al4V samples, in as-received condition and thermally treated, were analyzed with Scanning Kelvin Probe (SKP) to obtain potential maps of the surface. A plane-ended cylindrical Ni-Cr probe with a diameter of 50 μm was used as needle, moved with three stepping motors for x, y and z directions. All areas were performed stepwise and fully

automated, while the sample/needle distance was defined manually before the start of the scan. Measurements were performed over a scanned area of $3 \times 3 \text{ mm}^2$ in a humid environment of 98.5 % RH. Before measuring, the Kelvin probe was calibrated by using a standard Cu/CuSO₄ solution to establish a relation between the work function and corrosion potential. SKP potentials are given relative to the potential of the standard hydrogen electrode (SHE).

The SECM experiments were carried out using a CH900 scanning electrochemical microscope (CH Instruments, Austin, TX, USA). The electrochemical instrument was a sensolytics bipotentiostat. 5 mM potassium ferrocyanide was added to a 0.1 M KCl solution to act as an electrochemical mediator at the tip. The tips for the SECM studies were glass insulated, disk-shaped Pt microelectrodes, 25 μm disk diameter, manufactured from Pt wires (Goodfellow, Bad Nauheim, Germany). The oxidation of ferrocyanide at the Pt microelectrode was used to obtain the diffusion limit current. For that, the cyclic voltammogram was drawn from -0.25 V to 0.6 V vs. Ag/AgCl at 0.1 V s^{-1} and the potential reached at the maximum current was chosen to be applied to the tip (Figure 4). The potential of the tip was held at $+0.4 \text{ V}_{\text{vs. Ag/AgCl}}$ that corresponds to the current needed to enable the diffusion limited to the oxidation of ferrocyanide at the tip, I_{Lim} . The microelectrode was approaching the surface until touching. At that moment, it was 10 μm away from the surface. Experiments were performed by maintaining this Z position constant, and moving the Pt tip along the X and Y axes to record the current maps of the selected surface. Images were obtained by moving the microelectrode in a comb-type motion. The scan rate was 5 $\mu\text{m/s}$. The x-y scan was 1000 μm x 1000 μm , and with 5 μm step.

The SECM images were drawn using the dimensionless current ($I = i/i_{lim}$), where i_{lim} is the limiting current when the tip is far from the surface.

3. Results

3.1 Characterization of oxidized Ti6Al4V samples

Figure 5 shows the AFM images of the topography, 3D images and height line profile (5 μm x 5 μm) of Ti6Al4V surfaces before fretting-corrosion tests in as-received condition (a) and thermally treated at 500 °C (b) and 700 °C (c) for 1h. AFM images show important differences in the morphology of the surfaces.

The first important feature observed in the AFM images is related to the changes in the morphology of the surface as a consequence of the oxidation treatment. The topographical images of the Ti6Al4V in as-received condition (Figure 5a) show a smoother surface than that obtained in the oxidized samples. The Ti6Al4V surface, after oxidation treatment at 500 °C for 1h (Figure 5b), shows the incipient oxide nuclei that completely cover the surface. The preoxidized Ti6Al4V surface, at 700 °C for 1h, appears completely covered with globular oxides (Figure 5c).

The 3D images show significant changes in the surface roughness of the samples. The oxidation treatment of the Ti6Al4V samples leads to a variation in the surface nano roughness. Ti6Al4V in as-received condition shows a relative flat surface of about 20 nm. The oxidation treatment causes the formation of peaks and valleys (3D images in Figure 5b) associated with the growth of the oxide scale. This feature is more evident as the oxidation temperature increases (3D images in Figure 5c). The morphological changes are associated with higher nano roughness values obtained from the height line profile. After oxidation treatment, RMS value increases from 20 nm (as-received) to ≈ 30 and ≈ 160 nm,

for 500 °C and 700 °C, respectively (Figure 5). The surface modification as a consequence of the oxidation treatments has already been seen with roughened Ti6Al4V samples by the authors in previous works [27].

The thermal oxidation of the Ti6Al4V alloy gives rise to a modified surface whose composition and crystalline order is changed. XRD patterns of the Ti6Al4V samples after oxidation treatment at 500 and 700 °C for 1 h appear in Figure 6. All the oxidized samples exhibit α -Ti and β -Ti peaks at different diffraction angles corresponding to different crystallographic planes due to the penetration of X-rays beyond the oxide layer. Nevertheless, diffraction angles of Ti peaks shifted slightly left from their original positions. The XRD patterns performed on samples treated at 700 °C (Figure 6) revealed that the globular oxides observed by AFM in Figure 5c principally consisted of rutile, without any evidence of aluminum oxide.

Figure 7 shows the Vickers microhardness performed on the as-received and oxidized Ti6Al4V surfaces. It can be seen that microhardness is high at the lowest depth and decreases as depth increases. In addition, microhardness at the Ti6Al4V samples, thermally treated at 700 °C, is higher than those obtained for 500 and as-received surfaces, respectively. That is, rutile globular nodules formed at 700°C on the Ti6Al4V samples provide harder surfaces. Analogue results have been obtained by nanoindentation experiments (Figure 7) at the lowest depth (1000 nm).

The modified surfaces also promote changes in the electrochemical reactivity of the modified surface. Figure 8a shows the potential maps of surfaces before fretting-corrosion tests for as-received and thermally treated samples. The electrode potential is positive for all the samples thus indicating their passive behaviour. Nevertheless, the potential scale in

the plots varies in a range of approximately 100 mV in as-received condition, in comparison with those obtained after oxidation treatments of no more than 25 mV, thus indicating that the oxides provide a surface with a more uniform and stable potential distribution.

The average potential value in the as-received Ti6Al4V surfaces was around 120-140 mV. However, in the case of the oxidised Ti6Al4V samples, the potential values increase notably after thermal treatment, showing more positive values of 330 and 400 mV, for 500°C and 700°C, respectively. The SKP results demonstrate that increasing the oxidation temperature moves the potential values towards more positive values owing to the growth of rutile scale.

Additional information is obtained from the scanning electrochemical microscope. Current maps registered on Ti6Al4V surfaces before fretting-corrosion tests, in as-received condition and thermally treated at 500 °C and 700 °C appear in Figure 9a. An important aspect of these images is the extremely homogeneous current distribution. Images show a rather flat mapping of the Ti6Al4V surface in as-received condition and the thermally treated Ti6Al4V surfaces, with i/i_{lim} values between 0.2 and 0.6.

3.2 Fretting-corrosion tests

3.2.1 Characterization of Ti6Al4V samples after fretting-corrosion test

The simulator connected to the load machine allows us to apply the load profile versus time that appears on Figure 3, simulating normal walking for most patients [25]. In the fretting-corrosion tests carried out for 1 million cycles at 4 Hz with maximum normal contact pressure of 10 MPa, bone specimens (pins) moved from 95 to 120 microns against the Ti6Al4V disks in as-received condition and after oxidation treatment in 10% bovine serum

for 21 hours. The general examination of each metallic and bone sample after fretting-corrosion tests revealed differences.

Figure 10 shows the AFM images for Ti6Al4V samples, in as-received condition and oxidized at 500°C and 700°C, a), b) and c), respectively, after fretting-corrosion tests. The surface roughness in Ti6Al4V as-received condition after fretting-corrosion is lower and smoother than samples without fretting (compare Figures 5 and 10). The RMS value is reduced from 20 nm to 9 nm. After fretting-corrosion tests, the morphology of the surface has changed. Figures 11 show the cortical bone surface before and after fretting-corrosion tests against Ti6Al4V samples in as-received and at 700°C conditions. The bone after fretting-corrosion against the Ti6Al4V sample in as-received condition (compare Figure 11a and b) shows metallic contamination. The examination by SEM of the worn metallic surface in as received condition reveals scratches whose metallic particles produced are adhered on the bone surface.

With respect to the oxidized samples, the sample treated at 500° C has deeper wear because the RMS value is also reduced from 30 nm to 17 nm. Furthermore, white particles can be seen on the surface. The analysis by EDAX (data not shown) of these white particles is compatible with bone fragments resulting from the fretting-corrosion test. The abrasion produced in the fretting-corrosion test causes the presence of bone particles on the surface (Figure 10b). This feature could be indicating that the oxidized Ti6Al4V surfaces have increased their fretting resistance against bone. As a consequence, bone is worn and so produces particles (Figure 10b) that remain on the oxidized metallic surfaces.

Finally, AFM images of the thermally treated Ti6Al4V samples at 700°C presented a lower roughness (from 160 to 100 nanometers) and smoother surface than the same sample before

fretting-corrosion test (Figure 10c). Nevertheless, the globular oxides can still be observed without defects and no broken scales are observed. The examination by SEM of samples oxidized at 700 °C after fretting-corrosion tests did not reveal scratches on the surface. This behavior demonstrated that the oxide obtained in this condition resists the fretting-corrosion test. The cortical bone after fretting-corrosion is worn (compare Figure 11c and d).

These results indicate that in the fretting-corrosion mechanism of Ti6Al4V, the cortical bone is able to wear the metallic surface, however, if this Ti6Al4V is oxidized, the modified surface is able to wear the bone.

The next step was to study if the worn surface is more electrochemically reactive than those that have not been subjected to fretting-corrosion. Figure 8b shows the potentials maps by SKP of the worn surfaces in as-received and oxidized samples after fretting-corrosion tests. The potential maps obtained for all Ti6Al4V samples show a potential shift towards less positive values than before friction-corrosion test (compare Figure 8a and b). This seems to indicate that the friction alters the oxide surface. However, only the as-received samples show negative potential maps (≈ -50 and -70 mV) indicating that in this case, the native passive film formed on this sample has been destroyed and a more defective layer has been formed. This result confirms the poor tribological property of the passive film formed on titanium alloys [6].

Comparing these results with those obtained for worn oxidised 500°C and 700°C Ti6Al4V surfaces (Figure 8a and b) it can be observed that the potential values slightly decrease after the fretting-corrosion tests (from 330 to 160 mV and from 400 to 300 mV for 500°C and

700°C, respectively). This behaviour shows that the oxidized surfaces protect and resist the wear caused by the fretting-corrosion test better than the native passive film.

These results indicate that the oxide grown at 700 °C in the fretting process with human bone and in a physiological environment is more stable and more friction resistant than the other samples.

Figure 9b shows the current maps obtained for all Ti6Al4V surfaces after fretting-corrosion tests. The current maps obtained for Ti6Al4V samples in as-received condition show a slight increase of i/i_{lim} values (from 0.6 to 0.7) for not worn and worn samples, respectively. Considering that the current map has been recorded at the same distance between tip and surface, the increase in the current value may be associated with the higher reactivity of the surface, already established by the potential maps. This behavior could be associated with the breakdown of the passive film formed naturally on the Ti6Al4V alloy in as-received condition during the fretting-corrosion tests, and the subsequent formation of a defective passive film. Analogous behavior was observed for samples treated at 500 °C and 700 °C, in which the current maps also show an increase of the current values (from 0.5 to 0.9 and from 0.4 to 0.45, for 500 °C and 700 °C, respectively, Figure 9a-b). The greater increase of current values appears for the sample treated at 500°C, indicating that the oxide scale formed on the oxidized surface is not resistant enough and the oxide scale can be broken. Current maps of as-received and 500 °C conditions show some spots of current that some authors have associated with the formation of the instantaneous metastable pits when polarization is applied [28]. However, these fluctuations can also be due to the more heterogeneous surfaces obtained after the fretting-corrosion tests.

The characterization of the worn oxidized surfaces at 700 °C for 1 h after fretting-corrosion tests have demonstrated that the rutile scale supports the fretting-corrosion process due to the harder scale formed in comparison with the native passive film in the as-received condition and after oxidation treatment at 500°C.

4. Discussion

It is known that the use of thermal oxidation treatment for Ti alloys is designed to obtain in situ ceramic coatings, mainly based on rutile that can offer thick and highly crystalline oxide scales that are accompanied with the dissolution of oxygen beneath them [20].

The oxidation treatment at 500 °C is not high enough to generate thick oxide scales but the oxidation produces modifications in the outer layers, as the deviation in the Ti peaks in XRD diffractograms revealed (Figure 6). López et al. [29] assigned a small shift of the XRD's peaks corresponding to TiO₂ towards lower Bragg angles for TiNbZr oxidized samples. This displacement was associated with an increase on the TiO₂ lattice parameter produced by the presence of Zr and Nb atoms. Yan and Wang [30] established that the low hardness of untreated CP-Ti is due to its relatively low *c/a* ratio whereas the increase in hardness after thermal oxidation treatment is due to the lattice distortion caused by the dissolved oxygen which is reflected by the increase in the *c/a* ratio. In our case, the displacement of the diffraction angles of Ti peaks slightly towards the left from their original positions has likely been caused by the ingress of oxygen atoms in the subsurface zone (namely oxygen hardening layer) that triggers a slight increase in the hardness of the outer surface (Figure 7).

The absence of alumina in the XRD results could be attributed to the thermal oxidation treatment that was applied for just 1 hour. This short oxidation time does not allow the low

aluminum content to diffuse from the matrix to the surface. The addition of aluminium to titanium enhances the oxidation resistance since aluminium reduces the amount of oxygen dissolved in α -Ti [31]. The solubility of oxygen in titanium can be reduced from 34 % to 0.3 % at 700°C. Furthermore, it is reported [22] that the addition of vanadium suppresses the formation of an alumina barrier, which implies that vanadium reduces the aluminium activity in the Ti6Al4V alloy. Therefore Al_2O_3 would be unlikely to develop at the TiO_2 /substrate interface. This could explain the fact that the alumina scale was never observed at the oxide/substrate interface.

The surface modification promotes a higher nano roughness (figure 5) that does not induce a higher reactivity of the oxidized surfaces. Barranco et al. [30] reported similar corrosion behaviour of Ti6Al4V alloy at different roughnesses when samples were thermally treated at 500 and 700° C for 1 h. The authors demonstrated through the anodic polarization curves that the thermally treated Ti6Al4V surface at 700° C for 1h showed wider passive regions which reduced the susceptibility to pitting corrosion.

Fretting wear studies and sliding wear studies performed on Ti-35Nb-6Zr-5Ta showed that the mechanism of particle detachment is related to plastic deformation of superficial layers and formation of a tribological transformed layer (TTS) below the wear track. The formation of TTS was ascribed to deformation-induced transformation and this layer was formed of ultra fine grains of α -Ti with no β phases. The fretting test performed on three titanium alloys also had similar results [32]. The fretting tests on two $\alpha + \beta$ alloys Ti64, Ti5V3Al3Cr3Sn and β alloy Ti15V3Al3Cr in air resulted in the formation of particles and a hard tribological transformed structure that consisted of ultra fine grains α -Ti (20–50 nm diameter). The resultant wear particles were seen to oxidize quickly at the interface leading

to third body abrasive wear. Scanning electron microscopic investigation of the worn surfaces suggested that wear was due to abrasion, plastic deformation and cracking. In our case, the wear of the Ti6Al4V surfaces in as-received and oxidized at 500 °C conditions gave rise to particle detachment leading to third body abrasive wear and the adhesion of metallic particles to the bone counterpart, but the formation of the TTs was not analyzed in this work.

Thermally oxidized Ti6Al4V alloy at 700 °C exhibits a significant increase in hardness (Figure 7) due to the formation of rutile hard scale, verified by XRD, and the strains evolved during the dissolution of oxygen beneath the oxide layer of the substrate. The low hardness of close-packed hexagonal alpha-Ti is related to its relatively low c/a ratio. In the diffusion layer, the c/a ratio increases because of the lattice distortion caused by the dissolved oxygen, which leads to the increase in hardness (Figure 7) [31]. This information supports the absence of scratches on the oxidized samples and so the highest wear resistance obtained in Ti6Al4V samples thermally treated at 700 °C by 1h. In addition, the samples oxidized at 700°C showed the lowest electrochemical reactivity before and after the fretting-corrosion tests indicating that the surface is not only able to withstand the fretting-corrosion tests but also the electrochemical behavior and so the ion release is maintained in low ranges.

5. Conclusions

Oxidation treatment at 700° C for 1 h promotes the formation of a protective globular nano roughness oxide scale which mainly consisted of rutile without Al oxides detected. The globular oxides gave rise to the highest potential values by SKP and a homogeneous distribution of the current mappings obtained by SECM.

The characterization of the worn surfaces after the friction-corrosion process revealed that cortical bone is able to wear the Ti6Al4V surface in as-received condition, giving rise to a decrease in potential and an increase of current after fretting-corrosion. However, the oxidation treatments promote modified surfaces that are more friction resistant. Even more, the results of this work indicate that the hard oxide grown on Ti6Al4V at 700°C is the most electrochemically stable and friction resistant than the Ti6Al4V surfaces in as-received or oxidized at 500°.

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